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(21) International Application Number: PCT/US98/23640 (22) International Filing Date: 6 November 1998 (06.11.98) (30) Priority Data: 60/064,742 7 November 1997 (07.11.97) US (71) Applicant (for all designated States except US): MICROFLEX MEDICAL CORP. [US/US]; P.O. Box 32000, Reno, NV 89533-2000 (US). (72) Inventors; and (75) Inventors/Applicants (for US only): SAKS, Nathan, M. [US/US]; 127 Woodland Avenue, Reno, NV 89533 (US). BAKER, Jason, A. [US/US]; 5385 Vista Ridge, Reno, NV 89533 (US). ALDAPE, Fortunato, G. [US/US]; 5811 Shadow Park Drive, Reno, NV 89523 (US). GLENN, James, S. [US/US]; 1601 Foster Drive, Reno, NV 89509 (US). (74) Agents: OLDHAM, Scott, M. et al.; Oldham & Oldham Co., L.P.A., 1225 W. Market Street, Akron, OH 44313 (US).	(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>	
(54) Title: ELASTOMERIC ARTICLES FROM A BLEND OF POLYCHLOROPRENE AND ACRYLONITRILE (57) Abstract Shaped elastomeric articles such as gloves, condoms and breather bags, are prepared from a polymer blend composition comprising about 10 to about 90 parts by weight of a chloroprene polymer and about 10 to about 90 parts by weight of a nitrile polymer, based on 100 parts by weight of total polymer. The cured article has a thickness of 0.05 to 50 mils, a tensile strength of at least 9 MPA and an elongation of at least 300 %. The article, when stretched to fit over a human body member such as a hand, exerts an initial pressure, but thereafter relaxes to exert a reduced pressure which is no less than 50 % of the initial pressure. This invention provides a blend of a polychloroprene and a nitrile polymer that yields products of equivalent or similar feel and functionality compared to the common natural rubber latex glove. These products provide equal or better feel than nitrile or vinyl gloves currently available.		

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ELASTOMERIC ARTICLES FROM A BLEND OF POLYCHLOROPRENE AND ACRYLONITRILE

Field of the Invention

- 5 This invention relates to shaped elastomeric articles, in particular to gloves, condoms and breather bags, and to polymer blends and polymer blend compositions useful in the preparation of such articles.

Background of the Invention

- 10 Elastomeric examination and surgeon's gloves as well as condoms and breather bags, dipped products (i.e., finger cots, catheters, balloons) and cast products (i.e., tourniquets, sheeting) are currently made from several different polymers. Non-natural rubber latex products have been developed to address the issues related to natural rubber latex allergy. These current materials lack
15 the appropriate properties necessary to serve as a suitable substitute for natural rubber latex. In addition, individual polymers have specific chemical compatibility problems that limit their application in broad markets including health care, laboratory, emergency medical services and food handling.

- One such surgical glove is that described in U.S. Patent No. 5,014,362 to
20 Tillotson et al. and in Re. 35,616, which is a reissue of U.S. Patent No. 5,014,362. The glove described therein is a nitrile elastomer glove. More precisely, "nitrile elastomer" is a carboxylated nitrile-butadiene elastomer. The material of the Tillotson glove has a relatively low resilience; when a glove made of such material is stretched, the stress (i.e., pressure or force per unit area)
25 exerted by the material quickly drops from its initial value. In other words, the material has a high permanent set.

Summary of the Invention

- This invention provides a blend of a polychloroprene and a nitrile polymer
30 that yields products of equivalent or similar feel and functionality compared to the common natural rubber latex glove. These products provide equal or better feel, comfort and fit than nitrile or vinyl gloves currently available.

The invention further provides elastomeric films and shaped articles in film form, which are obtainable from the foregoing polymer blends on vulcanization or curing. Preferred shaped articles include gloves, condoms and breather bags and other dipped products.

5

Advantages of the Invention

The polychloroprene and nitrile blended gloves, condoms and breathing bags of the invention are made from synthetic elastomers and are free of allergenic latex proteins. They are made using processes similar to current manufacturing processes and techniques. The products are resistant to oxygen and ozone. Such blends yield films that have greater elongation and quicker film rebound compared to the current nitrile or vinyl products available. The blend is also softer at lower temperatures compared to current nitrile products available. The blend is more gasoline and oil resistant than current polychloroprene products available. It is also less permeable to gases than current natural rubber latex products available.

Tactile and physical properties of elastomers and gloves of this invention are similar to those of natural rubber latex and are better than those of other latex derived synthetic elastomers. Materials and articles of this invention have good chemical and puncture resistance, similar to those of other synthetic materials and better than those of natural rubber latex. In essence, materials and articles of this invention have all of the benefits of synthetic materials, and articles, e.g., good chemical resistance, good puncture resistance and no known allergens, and yet feel like natural rubber latex. Materials and articles such as gloves of this invention maintain a greater percentage of initial stress over time than do nitrile elastomers and articles made therefrom. In other words, they undergo less relaxation. Nitrile elastomers have a high modulus and lower elasticity so that gloves made therefrom may cause hand fatigue, in contrast, gloves made from elastomers of this invention minimize hand fatigue. Nitrile elastomers also have a permanent set, so that the materials loses resiliency and elasticity the longer it is stretched. Materials of this invention are more like natural rubber latex than nitrile elastomers in this regard. Another advantage is

that materials and gloves of this invention have no unpleasant odor, while nitrile gloves have an unpleasant odor which may bother both users and patients (e.g., dental patients).

5 Brief Description of the Drawings

The objects and advantages of the invention will become apparent upon a further reading of the detailed description of the preferred embodiments in conjunction with the figures, wherein:

Fig. 1 is a graph comparing relaxation of stress over time in an elastomer latex material of this invention with prior art elastomer latex materials.

Fig. 2 is a bar graph showing puncture resistance in an elastomer latex material of this invention and in prior art elastomer latex materials.

Detailed Description of the Preferred Embodiments

15 The invention comprises elastomeric articles, in particular gloves, condoms and breathing bags constructed from a polychloroprene (or chloroprene polymer) and an acrylonitrile copolymer. The terms "polychloroprene" and "chloroprene polymer" are used herein to denote both poly(2-chloro-1,3-butadiene) homopolymer and copolymers of said 2-chloro-1,3-butadiene with one or more additional halogenated monomers. Thus, 2-chloro-1,3-butadiene, which is also known as chloroprene, may be copolymerized with one or more monomers selected from the group consisting of 2,3-dichloro-1,3-butadiene or 2,3-dibromo-1,3-butadiene, 2-chloro-3-bromo-3,3-butadiene, 2-bromo-3-chloro-1,3-butadiene and butadiene. The acrylonitrile copolymer is preferably a carboxylated copolymer of acrylonitrile and butadiene. However, acrylonitrile-butadiene copolymers which are not carboxylated are also useful. Carboxylation is obtained by copolymerization of acrylonitrile and butadiene with a small amount (typically less than 10%) of a monomer such as acrylic acid, or methacrylic acid, or an ester thereof, such as methyl methacrylate.

30 A polymer blend as herein described, together with additional ingredients will be described below, is vulcanized or cured to yield an elastomer in film form. The total blended film thickness is about 0.05 - 50 mils., preferably about 0.1-20

mils. The blended film is characterized as having a tensile strength of at least (i.e., equal to or greater than) 9 MPA, preferably at least 12.5 MPA, and an elongation equal to or greater than 300%, preferably at least 500%. The products are further characterized as having no latex protein allergens, low modulus, high elongation, good tensile strength, high puncture resistance, good UV (ultra-violet) resistance, good chemical resistance, and good film rebound.

The invention also comprises compositions and blending steps useful in producing blended elastomeric products of the types described above.

A general formula of an unvulcanized or uncured polymer blend composition according to this invention is set forth in Table 1. Ingredients other than the polymer blend shown in Table 1 may be conventional.

TABLE 1	
Ingredients	Parts per Hundred Rubber
Polymer Blend	100
Crosslinker	0.05 to 2
Vulcanization Accelerator (primary)	0.10 to 10
Vulcanization Accelerator (secondary)	0.10 to 10
Antidegradant	0.10 to 15
Pigment	0.01 to 5
pH Stabilizer	0.05 to 5
Surfactant Stabilizer	0.00 to 5
Emulsifying Agent	0.01 to 15
Reinforcing Filler	0.00 to 40
Softener	0.00 to 50
Defoamer	0.00 to 5

Polymer blending takes place prior to vulcanization.

In the practice of this invention, a dipping form of desired shape is dipped into either a single polymer blend latex bath containing a polymer blend composition as shown in Table 1, or into two separate polymer latex dipping baths, the first containing one of the polymers of the blend (say polychloroprene

copolymer), the second containing the other polymer (say the acrylonitrile copolymer). The desired polymer blend is formed on the dipping form in the latter case. A single bath is preferred. The dipping form is dipped into a coagulant bath and dried before it is dipped into a latex bath, whether a single
5 latex bath or two latex baths are used. The latex coated dipping form may be dipped into a warm water leach bath if desired. The latex coated dipping form (or former) is then heated in an oven to cure the polymer blend latex.

The shape of the dipping form governs the shape of the article obtained. A glove-shaped dipping form is used to obtain a polymer blend latex glove.
10 Similarly, a condom-shaped dipping form is used to obtain a condom, and a breather bag-shaped dipping form is used to obtain a breather bag. Alternatively, films of this invention can be made by casting. Known casting techniques can be used.

A polymer blend as shown in Table 1 above may comprise about 10 to
15 about 90 parts by weight of polychloroprene (homopolymer or copolymer) and about 10 to 90 parts by weight of acrylonitrile copolymer as described above.

The invention is summarized as an elastomeric film article (such as a glove) comprising a layer of elastomeric material which is constructed of a blend of about 10-90 parts by weight polychloroprene (homopolymer or copolymer) and
20 about 10-90 parts by weight acrylonitrile copolymer with a tensile strength greater than 9 MPA and an elongation greater than 300%. Preferred tensile strength is at least 12.5 MPA, and preferred elongation is at least 500%.

This layer of elastomeric material is substantially impermeable to water and water vapor, has a thickness such that it is capable of being stretched to fit
25 securely about a human body member and to conform to the configuration of said human body member, thereby exerting an initial pressure on said human body member, and then relaxing to exert on said body member a reduced pressure, greater than 60% of said initial pressure one minute after being stretched and greater than 50% of said initial pressure ten minutes after being
30 stretched. More particularly, this layer has a thickness from about 0.05 to about 50 mils., preferably from about 0.1 to 20 mils., and constitutes the entire thickness of the article.

More preferably the blend contains about 25-75 parts by weight polychloroprene and about 25-75 parts by weight acrylonitrile butadiene. More preferably the polychloroprene may comprise poly(2-chloro-1,3-butadiene) or a copolymer comprising 2-chloro-1,3-butadiene and one or more of 2,3-dichloro-1,3-butadiene, 2,3-dibromo-1,3-butadiene, 2-chloro-3-bromo-1,3-butadiene or 2-bromo-3-chloro-1,3-butadiene, or 1,3-butadiene. The acrylonitrile copolymer comprises a carboxylated copolymer of acrylonitrile and butadiene.

An elastomeric glove of this invention is characterized as having no latex protein allergens, low modulus, high elongation, high puncture resistance, high cut resistance, good UV (ultra-violet) resistance, good chemical resistance, and good film rebound. Elastomeric films, condoms and breather bags possess these same properties.

Polymer blend elastomers of this invention also exhibit greater oil and chemical resistance (especially to oils and non-polar hydrocarbons) than natural rubber latex and better dexterity compared to nitrile.

An important characteristic of elastomeric polymer blend films of this invention and articles (such as gloves) made therefrom is high stress retention (or low relaxation) when subjected to a strain (or deformation) which remains constant over time. A polymer blend film or article of this invention maintains greater than 60% of its initial stress after one minute and greater than 50% after 10 minutes.

Fig. 1 shows stress retention (as the percentage of initial stress) as a function of time (in minutes) for a polymer blend elastomer of this invention (denoted "NeoPro" in Fig. 1) and prior art elastomers, i.e., nitrile, vinyl and natural rubber latex. As Fig. 1 shows, the elastomer of this invention (NeoPro) had better stress retention than either of the other synthetic polymers. Only natural rubber latex exhibited better stress retention. Disadvantages of natural rubber latex, including allergenic tendencies, lower puncture resistance and lower oil resistance are well known.

Fig. 2 shows puncture resistance in polymer blend elastomers of this invention (denoted "NeoPro") and in selected prior art elastomers, i.e., vinyl, natural rubber latex and nitrile. Puncture resistance of polymer blend elastomers

of this invention and of nitrile elastomers are nearly equal. Both have far better puncture resistance than either vinyl or natural rubber latex.

Example of Best Mode Known to Applicant

Gloves can be made as follows. A latex material having the formula set forth in Table 2 is prepared. The referenced Parts Per Hundred Rubber (phr) are by weight and are based on dry material. Often, the material is in liquid form at various solid percentages by weight. The sulfur is a crosslinker, the zinc dibutyl dithiocarbamate is an accelerator, the zinc oxide is an accelerator and cure agent, the phenolic antioxidant is an antidegradant, the potassium hydroxide is a pH stabilizer, the stabilizing surfactant is a stabilizer and wetting agent, and the paraffin wax is a softener.

Clean porcelain formers are dipped into a coagulant comprising a mixture of calcium salts (i.e., calcium nitrate, calcium chloride), water and non-ionic surfactant and dried. Then the formers are dipped into the latex blend (Table 2). The latex coated formers are then leached dried and cured in an oven for 20 minutes at 235 degrees Fahrenheit. After curing, the coated formers may be leached once again in hot water and then dipped in a slurry containing water and slip agent and dried. The gloves are then stripped from the formers.

If a powder-free product is desired, further processing is required off line.

20

TABLE 2	
Ingredients	Parts per Hundred Rubber
Polychloroprene Polymer (Neoprene 750)	60.0
Acrylonitrile Polymer (Tylac 68073)	40.0
Sulfur	1.0
Zinc Dibutyl Dithiocarbamate	1.5
Zinc Oxide	5.0
Phenolic Antioxidant	1.0
Potassium Hydroxide	0.5
Stabilizing Surfactant(s)	3.0
Paraffin Wax	2.0

30

Neoprene 750 was obtained from DuPont Dow Elastomers L.L.C.,
Wilmington, Delaware. Tylac 68073 was obtained from Reichold Chemicals, Inc.,
Reserch Triangle Park, North Carolina.

- 5 This invention has been described with reference to the preferred
embodiments including a best mode and preferred embodiment. It shall be
understood that the foregoing description is by way of illustration and not by
limitation.

What is Claimed is:

1. A polymer blend composition comprising:
 - (I) about 10 to about 90 parts by weight of a chloroprene polymer and
 - (II) about 10 to about 90 parts by weight of an acrylonitrile copolymer;
- 5 said blend further comprising at least one crosslinking agent and at least one vulcanization accelerator;
 said blend being curable to an elastomer in film form having a tensile strength of at least 9 MPA and an elongation of at least 300%.
2. A polymer blend composition according to claim 1, wherein
- 10 said composition comprises about 25 to about 75 parts by weight of said chloroprene polymer and about 25 to about 75 parts by weight of said acrylonitrile polymer.
3. A polymer blend according to claim 1, wherein said composition comprises about 40 to about 75 parts by weight of said chloroprene polymer and about 25
- 15 to about 60 parts by weight of said acrylonitrile polymer.
4. A polymer blend composition according to claim 1, wherein
 said chloroprene polymer is polychloroprene or a copolymer of monomers comprising
 - (a) 2-chloro-1,3-butadiene and
 - 20 (b) at least one monomer selected from the group consisting of 2,3-dichloro-1,3-butadiene, 2,3-dibromo-1,3-butadiene, 2-chloro-3-bromo-1,3-butadiene, 2-bromo-3-chloro-1,3-butadiene and 1,3-butadiene.
5. A polymer blend composition according to claim 1, wherein
- 25 said acrylonitrile copolymer is a copolymer of acrylonitrile and butadiene.
6. A polymer blend composition according to claim 5, wherein said acrylonitrile copolymer is a carboxylated copolymer of acrylonitrile and butadiene.
7. A polymer blend composition according to claim 1, wherein said chloroprene polymer is polychloroprene or a copolymer of monomers comprising
 - (a) 2-chloro-1,3-butadiene and
 - 30 (b) at least one monomer selected from the group consisting of 2,3-dichloro-1,3-butadiene, 2,3-dibromo-1,3-butadiene,

2-chloro-3-bromo-1,3-butadiene, 2-bromo-3-chloro-1,3-butadiene, and 1,3-butadiene and said acrylonitrile copolymer is a carboxylated copolymer of acrylonitrile and butadiene.

8. A vulcanizate of a composition according to claim 1.

5 9. A vulcanizate according to claim 8, said vulcanizate being in the form of a film.

10. A vulcanizate according to claim 9, wherein said film has a thickness from 0.05 to 50 mils.

10 11. A vulcanizate according to claim 10, wherein said film has a thickness from 0.1 to 20 mils.

12. A vulcanizate according to claim 10, wherein said film has a tensile strength of at least 9 MPA and an elongation of at least 300%.

13. A vulcanizate according to claim 12, wherein said film has a tensile strength of at least 12.5 MPA and an elongation of at least 500%.

15 14. A shaped elastomeric article comprising a layer of elastomeric material (a) comprising a cured polymer blend composition, wherein said polymer blend composition prior to curing comprises about 10 to about 90 parts by weight of a chloroprene polymer and about 10 to about 90 parts by weight of a nitrile polymer, based on 100 parts by weight of polymer, and (b) has a tensile strength
20 greater than 9 MPA and an elongation greater than 300%.

15. A shaped elastomeric article according to claim 14, wherein said polymer blend composition prior to curing comprises about 20 to about 85 parts by weight of said chloroprene polymer and about 15 to about 80 parts by weight of said acrylonitrile polymer.

25 16. A shaped elastomeric article according to claim 14, wherein said polymer blend comprises about 40 to about 75 parts by weight of said chloroprene polymer and about 25 to about 60 parts by weight of said acrylonitrile polymer.

17. A shaped elastomeric article according to claim 14, wherein said nitrile polymer is an acrylonitrile-butadiene copolymer.

30 18. A shaped elastomeric article according to claim 17, wherein said nitrile-butadiene copolymer is a carboxylated acrylonitrile-butadiene copolymer.

19. A shaped elastomeric article according to claim 14, wherein said tensile

strength is greater than 12.5 MPA and said elongation is greater than 500%.

20. A shaped elastomeric article according to claim 14, wherein further said layer of elastomeric material (c) is substantially impermeable to water and water vapor, (d) has a thickness such that it is capable of being stretched to fit securely
- 5 about a human body member and to conform to the configuration of said human body member, thereby exerting an initial pressure on said human body member, and then relaxing to exert on said body member a reduced pressure, greater than 60% of said initial pressure one minute, after being stretched and greater than 50% of said initial pressure ten minutes after being stretched.
- 10 21. A shaped elastomeric article according to claim 20, said layer having a thickness from about 0.05 to about 50 mils.
22. A shaped elastomeric article according to claim 20, said layer having a thickness from about 0.1 to about 20 mils.
23. A shaped article according to claim 20, said article being a glove.
- 15 24. A shaped article according to claim 20, said article being a condom.
25. A shaped article according to claim 20, said article being a breather bag.

FIG. -1

Natural Rubber Latex vs. NeoPro vs. Vinyl vs. Nitrile

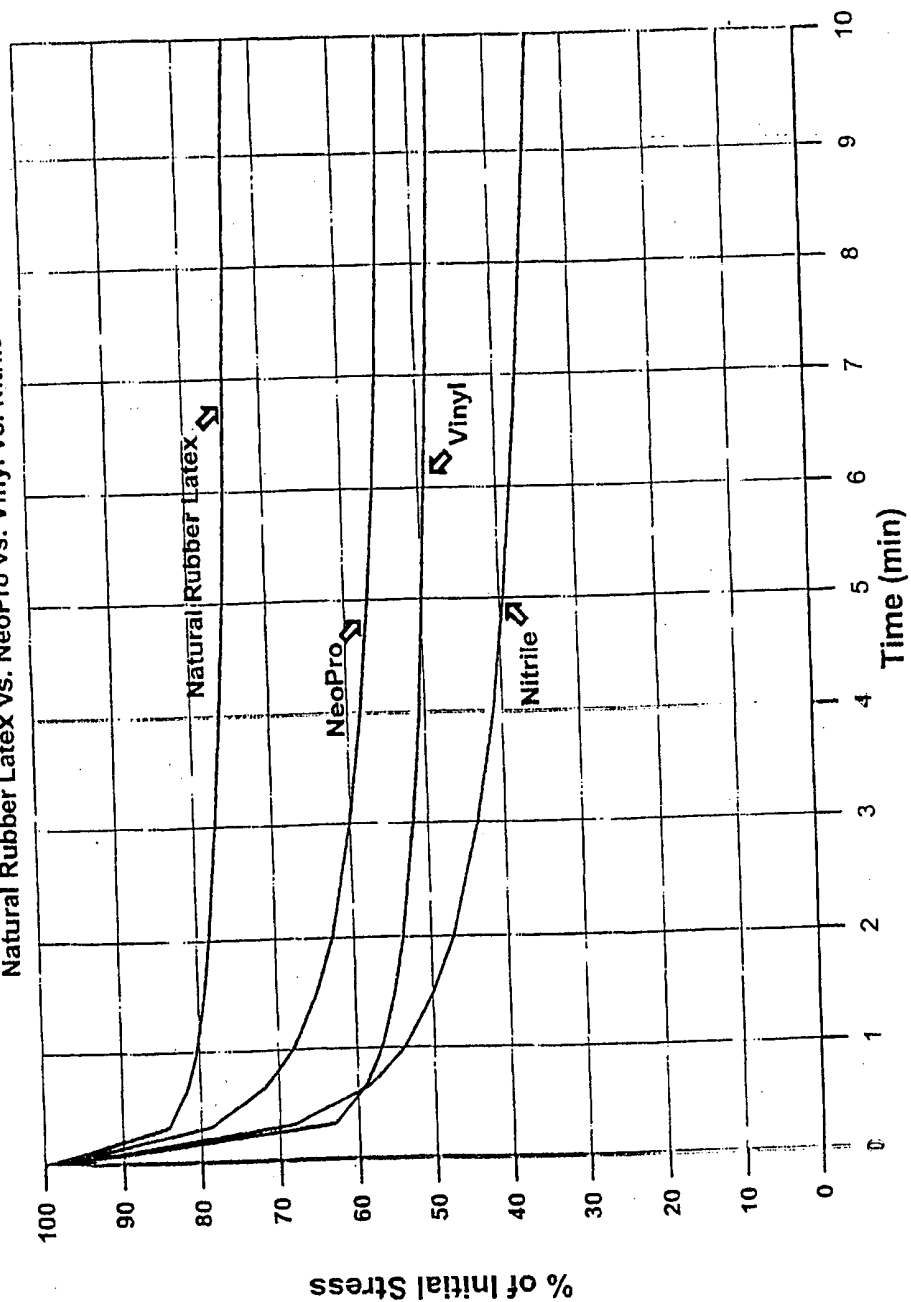
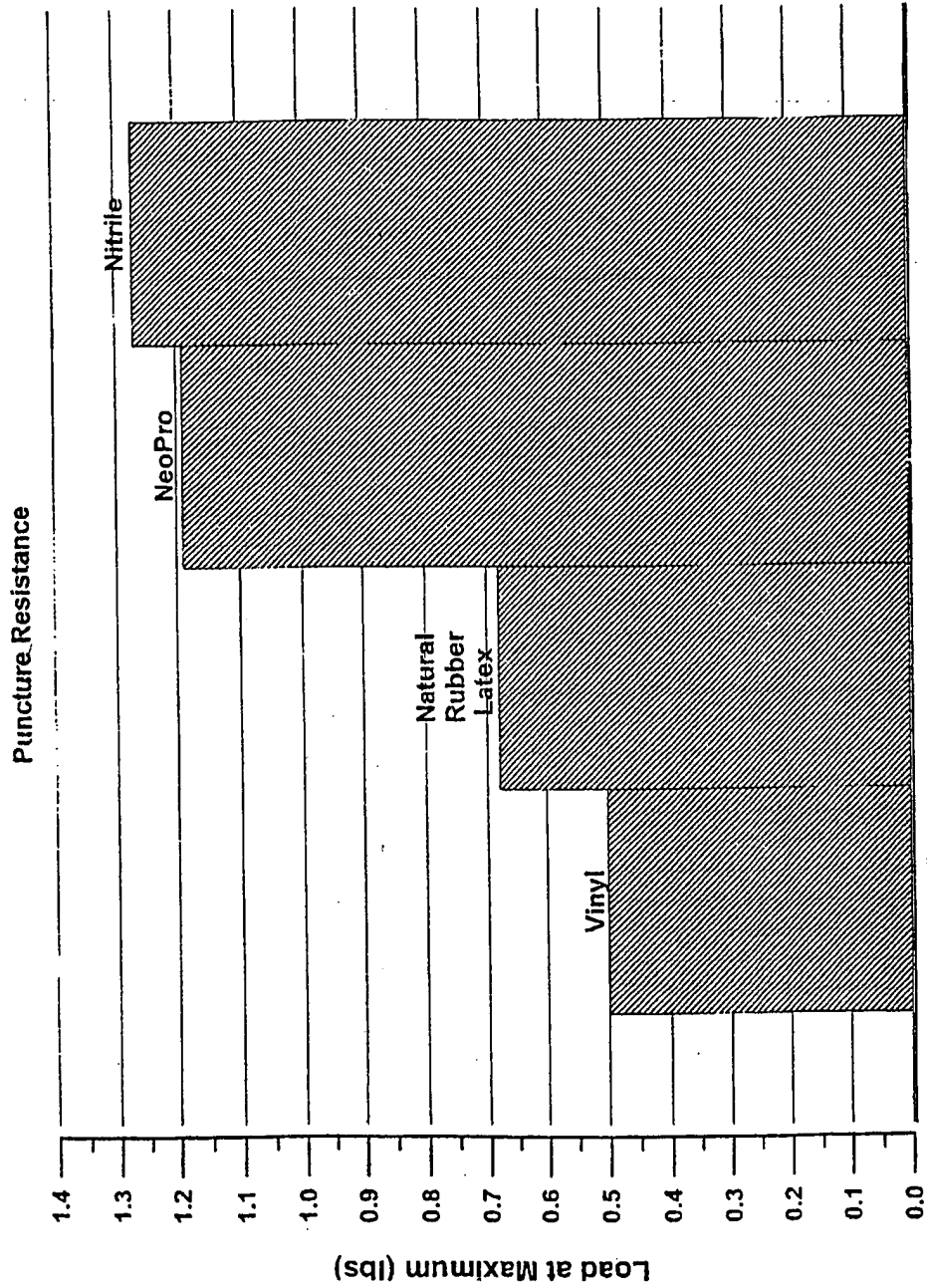


FIG. - 2



INTERNATIONAL SEARCH REPORT

International application No.
PCT/US98/23640

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :C08L 27/04
US CL :525/215, 330.9
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

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Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5,187,232 A (MUSCH et al) 16 February 1993, see entire document.	1-25
X	US 4,048,261 A (STARMER) 13 September 1977, see example III.	1-25
X	US 3,943,192 A (COULTHARD) 09 March 1976, see entire document.	1-25

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

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